

Spectroscopic and Laser Properties of
Cr:LiCaAlF₆ and Cr:LiSrAlF₆ Crystals

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SPECTROSCOPIC AND LASER PROPERTIES OF
Cr:LiCaAlF₆ AND Cr:LiSrAlF₆ CRYSTALS*

The natural fluoride mineral colquiriite (LiCaAlF₆ or LiCAF) and its strontium substituted analog (LiSrAlF₆ or LiSAF) have structural and growth properties that are essentially ideal for use as chromium-doped tunable lasers.¹⁻⁴ These crystals grow congruently at temperatures of 825°C (750°C), possess near unity distribution coefficients for chromium, and can accept high fractional substitutions of chromium. Laser quality crystals have been grown by Czochralski, Bridgman, and horizontal zone melting methods. Trigonal LiCAF (LiSAF) crystallizes in the space group P31c, and has but a single type of Al³⁺ octahedral site. Al³⁺ octahedra do not share fluorine ions, thus minimizing the pair formation and quenching of luminescence at higher chromium doping levels. The relatively low crystal field strength at the Al³⁺ site arising from the fluorine ligand results in ⁴T₂ as the first excited state of Cr³⁺. This results in broadband ⁴T₂ → ⁴A₂ emission at room temperature. Figures 1 and 2 show the room temperature, polarized absorption and emission spectra^{1,3} of LiCAF and LiSAF, respectively. These spectra are canonical for Cr³⁺ ions in a single, low-field octahedral site. Due to the higher static odd-parity site distortion in LiSAF, transition strengths in LiSAF are about three times larger than those in LiCAF. This difference is also reflected in the three-fold longer fluorescence lifetime of LiCAF (170 μsec) compared to LiSAF (67 μsec). The quantum yields for fluorescence at room temperature are essentially unity. The peak fluorescence emission cross section and saturation fluence for LiCAF

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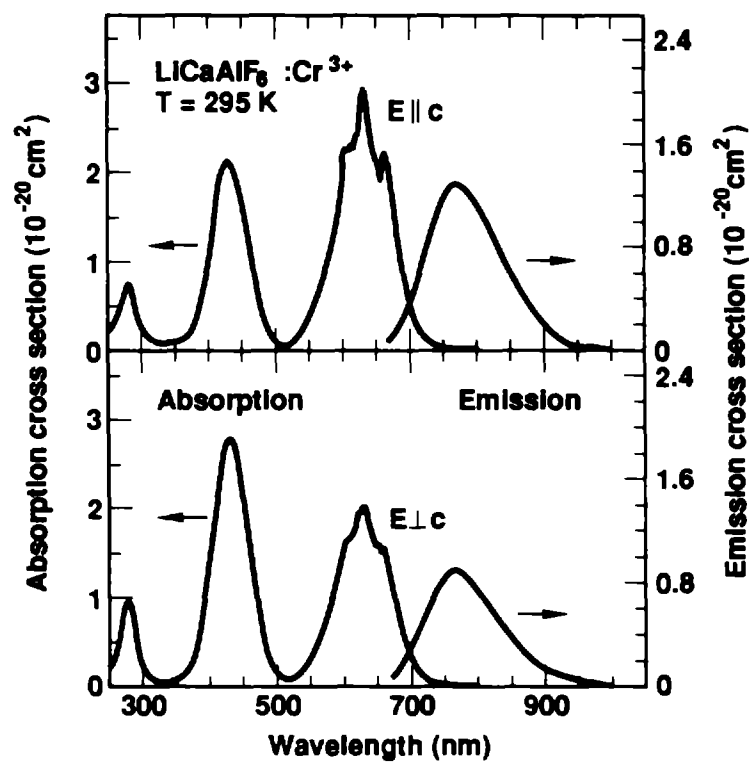


Figure 1. Absorption and Emission Spectra of Cr:LiCAF

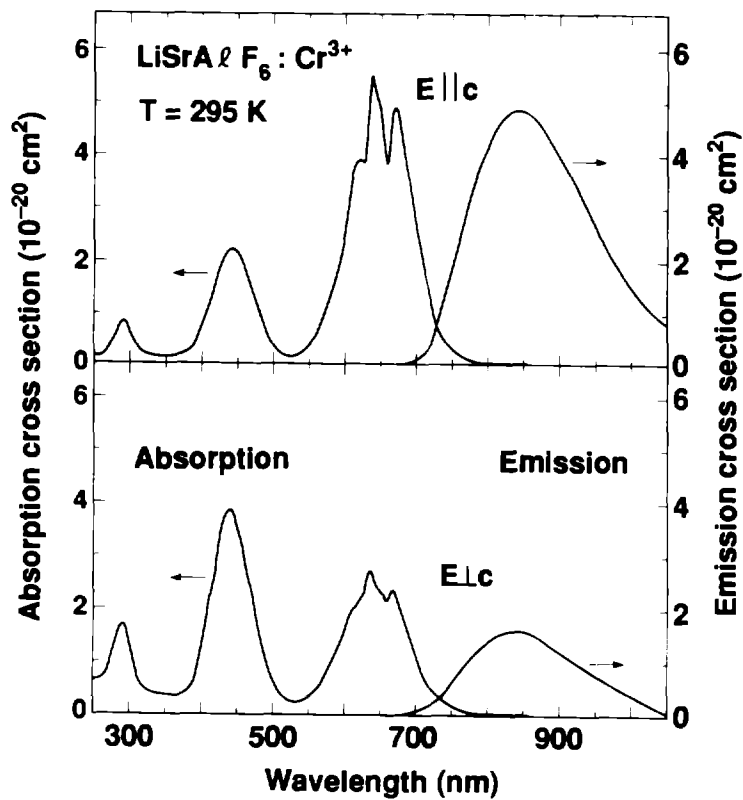


Figure 2. Absorption and Emission Spectra of Cr:LiSAF

(LiSAF) are determined to be 1.3 pm^2 and 20 J/cm^2 (5.0 pm^2 and 5 J/cm^2), respectively. These values are quite convenient for operating chromium tunable lasers pumped either by a flashlamp or by a Kr^+ laser.

The efficiency of chromium tunable lasers is often limited by excited state absorption occurring in the spectral region of fluorescence emission. Lattice structure and symmetry considerations² suggested that LiCAF would be relatively favorable with respect to ESA loss in a chromium laser. Direct ESA measurements² in Cr:LiCAF give a peak ESA cross section of 0.17 pm^2 . This value is much smaller than the peak emission cross section of 1.3 pm^2 , and the efficiency of a Cr:LiCAF laser should not be substantially reduced due to ESA processes.

Laser pumped Cr:LiCAF and Cr:LiSAF laser experiments^{1,3} were performed using a Kr^+ laser as the pump source. Figure 3 shows the measured laser output power as a function of absorbed pump power for LiCAF and several other chromium laser materials. Figure 4 shows similar data for Cr:LiSAF. The slope efficiency of LiCAF (52%) is seen to be identical to that of alexandrite, a laser material known for its high performance. The slope efficiency of Cr:LiSAF (36%) is noticeably lower than those of Cr:LiCAF and alexandrite. The different slope efficiencies of these lasers are, in part, due to differing passive losses in the experimental laser crystals. To remove this bias in comparison, it is appropriate to compare the intrinsic slope efficiencies^{1,3} of materials (slope efficiency in the limit that resonator output coupling is much greater than passive crystal loss).

To determine the intrinsic slope efficiency of a material, slope efficiencies are measured for several different values of output coupling fraction (output mirror transmission). Reciprocals of the measured slope efficiencies are plotted against the reciprocals of the output coupling fractions, as shown in Figure 5. The slope efficiency intercept at large output coupling gives the intrinsic slope efficiency. The values found are LiCAF (67%), LiSAF (53%), alexandrite (65%), YAG (25%), ScBO_3 (25%), and the fluoride garnet $\text{Na}_3\text{Ga}_2\text{Li}_3\text{F}_{12}$ (28%). The relatively high intrinsic slope efficiency values for LiCAF and alexandrite indicate relatively low excited state absorption losses in these materials. The materials with low intrinsic slope efficiencies of 25-30% are dominated

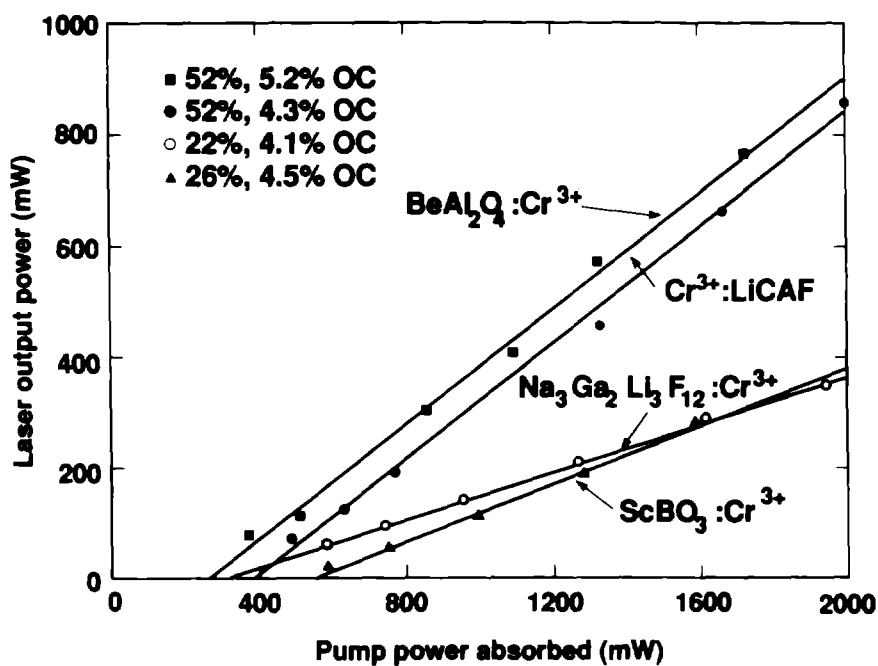


Figure 3. Laser Power Output vs. Absorbed Pump Power

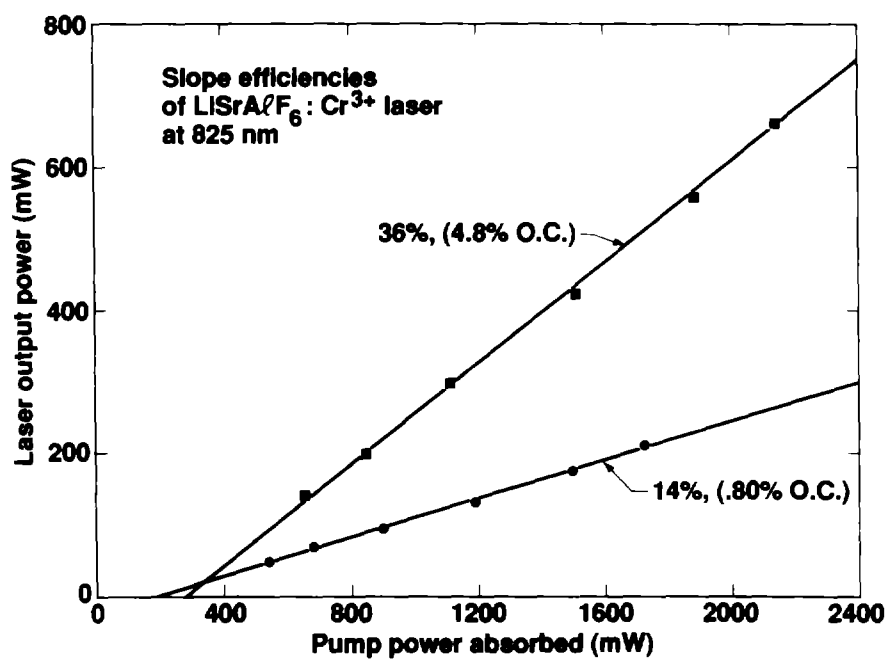


Figure 4. Laser Power Output vs. Absorbed Pump Power

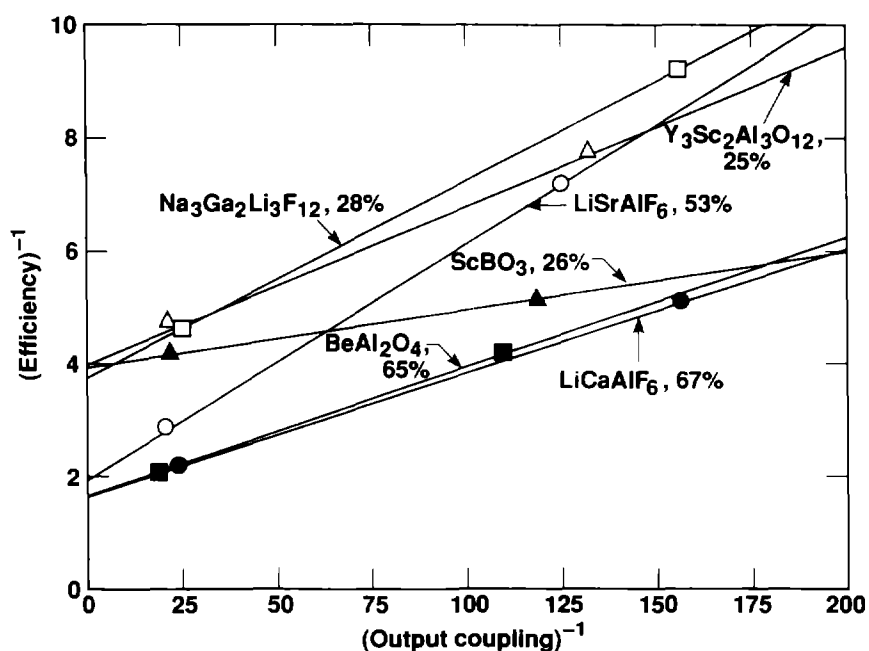


Figure 5. Reciprocal slope efficiency vs. reciprocal output coupling fraction. Intrinsic slope efficiency values are indicated.

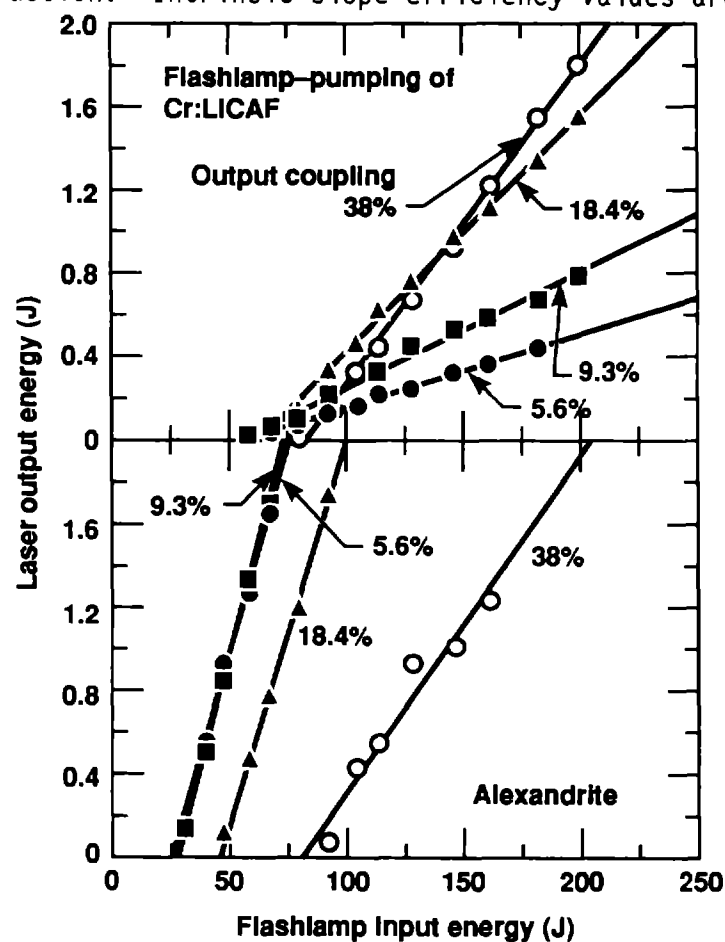


Figure 6. Laser output energy vs. flashlamp input energy for Cr:LiCAF and alexandrite laser rods. Output coupling mirrors with percent transmission of 5.6, 9.3, 18.4, and 38 were used.

by excited state absorption losses and cannot be rendered more efficient simply by reducing passive bulk crystal losses. LiSAF, with a 53% intrinsic slope efficiency, is inferred to have a somewhat higher excited state absorption loss than LiCAF (consistent with the larger Stokes shift of LiSAF).

Using a single-plate birefringent tuning element in the laser cavity, Cr:LiCAF and Cr:LiSAF crystals have been tuned over the spectral ranges 720-840 and 780-920 nm, respectively. These tuning ranges are red shifted from the nominal tuning range of alexandrite and provide practical tunable sources in these ranges.

The broad absorption bands of chromium in LiCAF, and the ability to dope LiCAF crystals with high concentrations of chromium without quenching fluorescence and destroying crystal optical quality, make Cr:LiCAF a likely candidate for efficient flashlamp pumping. A cylindrical Cr:LiCAF laser rod of 0.64 cm diameter and 8 cm length, doped with 1.8 mol% Cr³⁺, was prepared for flashlamp pumping experiments. A single ILC lamp (6.5 cm arc length, 4 mm bore diameter, 450 torr xenon) was coupled to the laser rod in a Kigre diffuse reflector pump cavity. The lamp drive was critically damped with an LC time constant of 108 microseconds at an energy of 280 joules. The laser resonator consisted of a highly reflecting concave mirror with a one meter radius of curvature and a flat output coupler, whose transmission coefficient was varied between 5 and 50%. Figure 6 plots the measured output energy as a function of flashlamp input energy for Cr:LiCAF and for a high quality alexandrite laser rod of similar dimensions. Data was taken for four different values of transmission of the output coupling mirror. A maximum output energy of 1.8 joules was obtained from the Cr:LiCAF rod for an input energy of 200 joules, with a slope efficiency of 1.5%. Using Findlay-Clay analyses of these data, we determined that the Cr:LiCAF laser rod had a rather high bulk crystal loss coefficient of 3.4% cm⁻¹. This value of loss coefficient was directly measured using an AlGaAs laser diode emitting at 780 nm. Using this loss data, we can calculate that a Cr:LiCAF laser with suppressed bulk crystal loss would produce free-running laser emission with a slope efficiency of 4.1%. Recent improvements in crystal growth have produced crystals exhibiting loss coefficients smaller by an order of magnitude than present in the

rod used in the flashlamp pumped experiments described above. Slope efficiencies approaching 5% are anticipated using laser rods made from the improved material. Achievement of the 5% figure will also require incorporating a luminescent spectral converter (Rhodamine 6G dye and Ce doped flashlamp) into the laser pump configuration, as determined by converter measurements made to date.

In conclusion, Cr:LiCAF and Cr:LiSAF have been found to be excellent materials for efficient, tunable, chromium lasers. Their physical, thermal, optical, and spectroscopic properties permit efficient laser emission at the watt level under laser pumping, tunable over the range 740-920 nm. Flashlamp pumping has generated joule level output energy without appearance of deleterious solarization effects. Further improvements in laser performance are anticipated as laser crystals of higher quality become available.

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